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MATERIAL COMPOSITION OF THE DUST FROM THE ELECTROSTATIC PRECIPITATORS OF A VANYUKOV FURNACE AT THE MIDDLE URAL COPPER SMELTER

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Results are presented from studies of the elemental and phase compositions of dust from the electrostatic precipitators of a Vanyukov furnace operated at the Middle Ural Copper Smelter The size and shape of the dust particles were evaluated and the dust's elemental composition was examined at local probe points. The results were generalized, and it was determined that there is a correlation between the copper and lead contents of the dust and between the copper and arsenic contents of the sulfide phases.
Keywords: *gases, fumes, composition, microanalysis, phases, structure.*

The dust which is formed in the autogenic smelting of copper-zinc concentrates in Vanyukov furnaces (VFs) varies in its chemical and phase compositions [1–3]. The composition of the dust is determined by the quality of the raw materials being smelted, the content of highly volatile metals and compounds in the charge, the volume of recycled materials that is used, and the design of the smelting furnace [4–7]. The phase composition of the dust depends on the composition of the gases that entrain it and the temperature regime in the dust-cleaning system. For example, in processes which are accompanied by the formation of sulfurous anhydride, sulfates are likely to be formed during simultaneous cooling of the dust and the gas. In contrast to the original raw material, the dust formed by the autogenic smelting of copper-zinc sulfide concentrates contains not only mechanically suspended particles of the charge materials but also high concentrations of lead (including volatilizable forms – Pb, PbS, PbO), arsenic (As_2O_3), antimony (Sb_2O_3), cadmium (Cd, CdO, CdS), and other elements. The gas formed in autogenic smelting contains SO_2, SO_3, O_2, CO_2, H_2O, N_2, and vapors of volatilizable compounds. Cooling of the gas together with solid particles from the dust-sized charge materials leads to the formation of oxides as a result of the partial oxidation of sulfides, sulfates (which are products of secondary reactions), and condensate.

In connection with the high content of valuable metals in the dust, it is important to develop an efficient technology that can extract copper, zinc, lead, sulfur, and precious metals for use in commercial products while also converting the hazardous elements (arsenic, chlorine, fluorine, etc.) into nontoxic forms suited for subsequent recycling. Having information on the forms in which different elements exist in gas-cleaning-system dust and on their microstructure is important for the creation of such technologies.

Gases from the Vanyukov furnaces at the Middle Ural Copper Smelter (SUMZ) are successively cooled and cleaned in a dust-cleaning system, waste-heat boiler, cooling tower (water spray), and electrostatic precipitator. The temperature of

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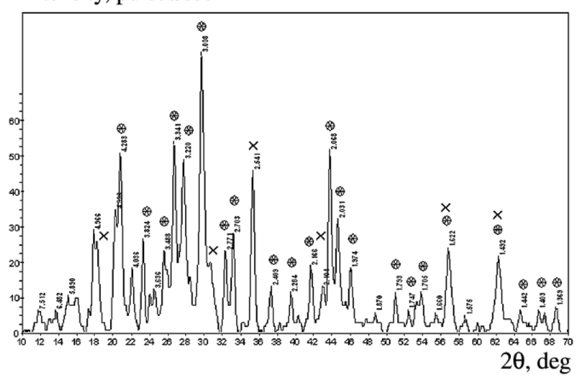

Fig. 1. Diffraction pattern of a dust sample from an electrostatic precipitator of a Vanyukov furnace: ⊕) $PbSO_4$; ·) Fe_3O_4.

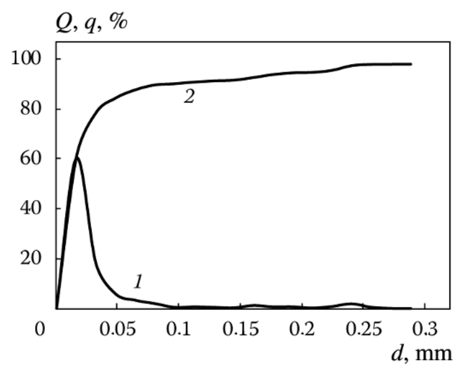

Fig. 2. Differential (*1*) and integral (*2*) size distributions of dust particles from an electrostatic precipitator of a Vanyukov furnace.

the dust-gas flow is such as to ensure that the metal structures of the equipment perform as intended and to prevent condensation of sulfuric acid. Most of the dust and the sublimates are removed in the precipitator and sent off for recycling [8]. The temperature regime inside the precipitator is kept within the range 350–450°C. The composition of the gases varies within the following ranges, vol.%: SO_2 20–30; SO_3 0.2–0.4; CO_2 13–23; CO 0.7–0.9; O_2 3–8; H_2O 15–27; N_2 – remainder.

The elemental and phase compositions of the precipitator dust were studied to substantiate the technology chosen for its subsequent recycling.

The investigated dust sample from the electrostatic precipitator at the SUMZ contained the following, %: Pb 11.8; Fe 13.3; Zn 11.7; Cu 10.3; S 9.0; As 5.81; SiO_2 0.48; CaO 0.36; Al_2O_3 0.21; Sb 0.44; Cd 1.00; Ni 0.004; Bi 0.26; F 0.001; 1.6 g/ton Au; 51.6 g/ton Ag. The results obtained from x-ray phase analysis showed (Fig. 1) that the main components of the dust are lead sulfate $PbSO_4$ and magnetite Fe_3O_4.

The dimensions and form of the dust particles were evaluated on a Camsizer-XT analyzer and a JSM-59000LV scanning electron microscope. The sample consisted of particles with a size of 0.001–0.30 mm (Fig. 2). The average values of their sphericity coefficient was 0.83 and the average value of their symmetry coefficient was 0.89. The diameter of 60.2% of the particles d = 0.001–0.017, and 90% of them had a diameter of less than 0.096 mm.

Local probing of the phases was done by the method of x-ray microanalysis on scanning electron microscope JSM-59000LV and energy-dispersive x-ray spectrometer OXFORD INCA Energy 200. The x-ray microanalysis of a particle (Fig. 3*a*) about 40 ∝m in size showed that it was comprised of an oxide component $(Fe, Cu, Zn)_2O_4$ and a silicate compo-

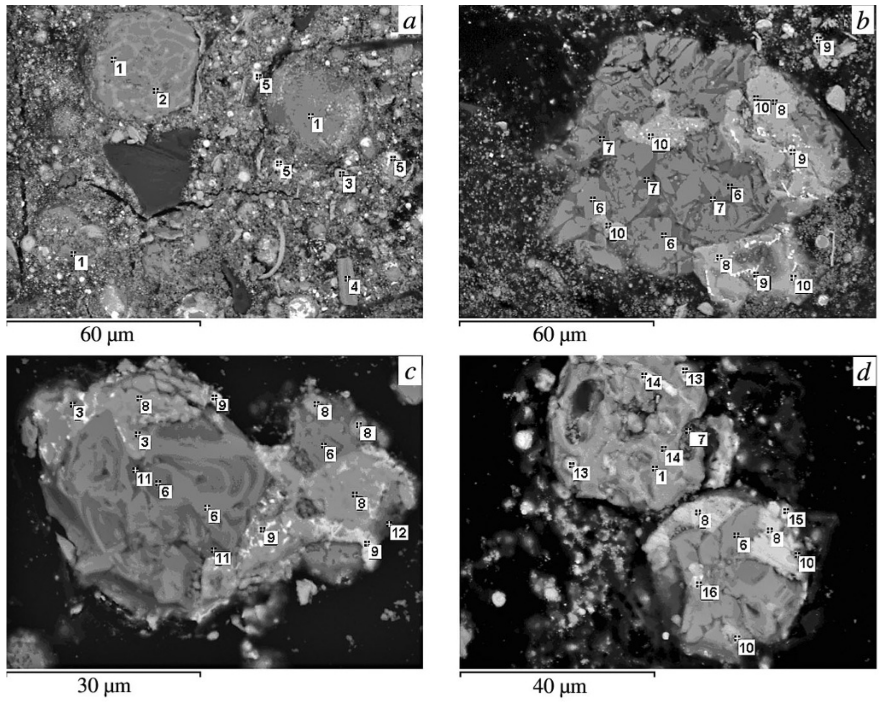

Fig. 3. Microstructure of dust particles from an electrostatic precipitator of a Vanyukov furnace and points where the phases were probed locally.

nent (Fe, Cu, Pb)$_2$SiO$_4$. Both the oxide phases and the silicate phases are solid solutions with substantial concentrations of Fe, Cu, and Zn. The silicates contain up to 16.3% lead and 3.9% arsenic. Another oxide particle consisted of a solid solution that was based on iron oxide (Fe, Zn, Cu)$_2$O$_3$ and contained impurities – up to 2.5% Pb and 0.6% Cd. The existence of silicate and oxide phases in the dust is probably related to the entrainment of slag particles during the smelting operation. The finer (smaller than 5–10 ∝m) dust particles are formed by sulfide phases (Zn, Fe)S and sulfate (based on lead sulfate) phases. The sulfate phases contain the following, %: Pb 34.1; Cu 18.7; Fe 8.0; Zn 5.4; As 6.0; Cd 1.7; Sb 1.6 (Table 1).

Some of the particles consist partially or completely of iron oxides (magnetite or wüstite). The magnetite contains up to 4.0% zinc and 3.6% copper (Fig. 3*b* and Table 1). Certain particles that were in contact with iron oxides were found to contain phases comprising solid solutions of silicates of iron and zinc [9]. Regions occupied by sulfide phases that are close in composition to bornite were seen in the analysis. These phases include small sections (point sections and sections in the form of chains) of sulfides of zinc and lead.

The other coarse (about 60 ∝m) particle was based on magnetite (Fig. 3*c*) and was next to a small section occupied by a calcium-bearing silicate phase (Ca, Fe)SiO$_3$. The iron oxide contained 0.7–3.6% Cu and 2.0–3.5% Zn, while the silicate phase contained 1.0–3.5% Cu, 8.5–10.5% Zn, 0.8–1.6% As, and up to 2.8% Pb. The sulfide phases were bornite, sphaelerite (Zn, Fe)S, sulfides of copper, and point inclusions of a solid solution based on lead sulfide PbS–Cu$_2$S–(Zn, Fe)S. The composition of the lead-bearing sulfide included the following, %: Pb 33.4–39.7; Fe 7.7–10.0; Cu 21.2–23.4; Zn 2.3–3.0; As 0.6–3.6; up to 0.7 Cd; 2.1 Sb.

Microanalysis of the next particles showed that were nonuniform in terms of both their structure and their composition (Fig. 3*d*). The iron oxides contained zinc (9.3%) and copper (8.4%), which are likely to form ferrites. The magnetite particles were fully formed and the boundaries of Fe$_3$O$_4$ particles were clearly visible. Some of the sphaelerite had high copper contents. Lead was distributed mainly over the surface of the particles, forming either oxide-sulfide phases or sulfate phases. The surface of the metallographic section contained fine copper phases, including 3.3–4.7% Fe, 0.6–1.1% Zn, 4.7–5.2% As, 0.9–1.4% Pb, and 1.7% Sb.

TABLE 1. Elemental Composition of Dust from the Electrostatic Precipitators of a Vanyukov Furnace at Locally Probed Points (see Fig. 2)

No. of point	Content, wt.%								Phases
	Si	S	Ca	Fe	Cu	Zn	Pb	As	
1	0–1.4	0	0	53.3–65.7	5.7–13.1	3.6–9.3	0–2.5	0	$(Fe, Cu, Zn)_2O_3$
2	8.3	0	2.6	22.9	17.2	2.9	16.3	3.9	$(Fe, Cu, Pb)_2SiO_4$
3	0–1.0	27.8–30.7	0	2.4–5.8	2.6–7.6	42.6–63.3	0–7.9	0	(Zn, Fe, Cu)S
4	0.7	0.2	0	77.0	1.0	0.0	0	0	FeO_x
5	0.2–0.7	11.5–16.1	0	2.4–8.0	9.3–26.5	1.5–5.4	34.1–60.0	0–6.0	Sulfates
6	0–2.9	0–0.8	0–0.7	62.9–73.5	0.7–3.6	1.5–4.0	0	0	Fe_3O_{4-x}
7	17.6–18.8	1.7–2.1	3.0–4.2	26.0–36.7	0.8–1.6	9.2–11.2	0	0.7–1.1	$FeSiO_3$–$ZnSiO_3$
8	0–1.0	15.6–24.8	0	3.3–19.3	54.9–69.5	0–5.7	0–2.8	0–1.0	Cu_5FeS_4
9	0–1.2	12.4–18.6	0–0.5	2.8–10.0	7.0–23.4	2.3–13.0	33.4–49.1	0–3.6	PbS–Cu_2S–(Zn, Fe)S
10	0–0.2	20.6–27.6	0	3.3–13.4	14.0–20.8	29.1–50.3	0–3.6	0	(Zn, Fe)S–Cu_2S
11	14.4–15.4	1.0–3.1	15.6–16.4	20.2–22.7	1.0–3.5	8.5–10.5	0–2.8	0.8–1.6	$(Ca, Fe)SiO_3$
12	0.5	2.8	26.2	2.5	4.9	0.7	4.2	0	$(Ca, Cu)CO_3$
13	0	0.3–2.1	0	3.3–4.7	78.6–83.1	0.6–1.1	0.9–1.4	4.7–5.2	Cu–Fe–As
14	6.8–11.0	0–0.9	3.3–4.5	10.7–20.5	1.5–4.7	23.9–29.3	9.3–20.5	0–1.0	$(Fe, Zn, Pb)_2SiO_4$
15	0.3	9.9	0	5.1	36.5	9.5	27.3	4.1	$(Cu, Pb, Zn)SO_3$
16	0.4	7.1	0	34.9	16.5	7.0	7.6	0	$(Fe, Cu, Pb, Zn)SO_4$

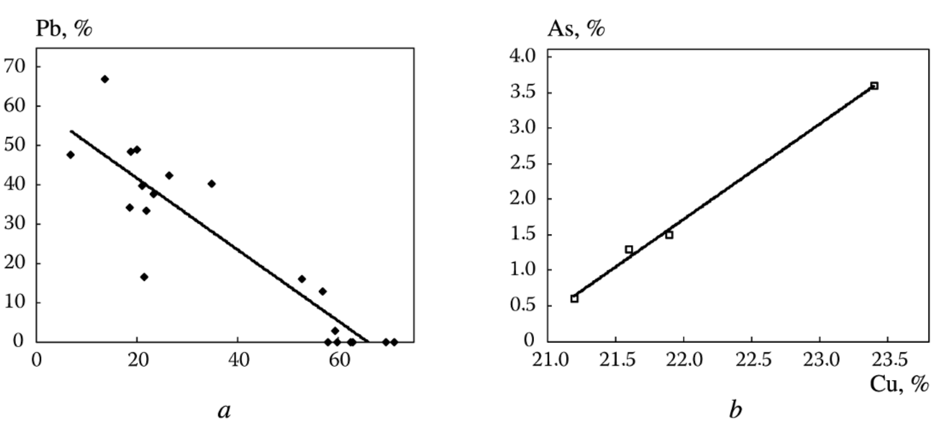

Fig. 4. Dependence of the contents of lead (*a*) and arsenic (*b*) in the sulfide phases of the dust particles on the concentration of copper in them.

In generalizing these results, we found a correlation between the contents of copper and lead in the sulfide phase; its enrichment with copper leads to a reduction in the concentration of lead (Fig. 4). There is almost no lead in the sulfides which have a copper content similar to that of bornite. We found a connection between the contents of copper and arsenic in the sulfides (see Fig. 4); an increase in the copper content of lead-bearing (33–40% Pb) sulfides within a narrow range of concentrations (21.0–23.5% Cu) leads to a linear increase in arsenic content.

Conclusions. The data obtained here make it possible to conclude that the electrostatic-precipitator dust from the smelting of copper-zinc concentrates in Vanyukov furnaces at the SUMZ is composed of a collection of particles (1–80 ∝m in size) that have undergone heat treatment in a gaseous medium (SO_2–N_2–CO_2–H_2O–O_2). The dust consists of the following:

• fine fractions of concentrate in the form of partially oxidized sulfide phases;

• mechanically entrained particles of matte and slag with magnetite inclusions;

• fine fractions of readily volatilized compounds condensed from the gas phase; the cooling of these compounds in gases having a high content of sulfur anhydride leads to the formation of sulfates of lead and zinc.

One distinctive characteristic of the dust is that it contains metals (Cu, As, Pb, Sb) which are reduced from oxides by the low-amplitude currents associated with the high-gradient (20–40 kV) field of the precipitator.

These findings will be used to develop a technology for separately recycling electrostatic-precipitator dust from Vanyukov furnaces and removing harmful impurities from the copper-smelting operation.

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